



Communication Polymeric Terbium(III) Squarate Hydrate as a Luminescent Magnet

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Abstract: Polymeric terbium(III) squarate hydrate $[{Tb_2(C_4O_4)_3(H_2O)_8}_n]$ was prepared from TbCl₃ or Tb₂O₃ and squaric acid. The crystal structure was determined in a monoclinic *Pc* space group, and the whole molecular arrangement gives a sandwiched two-dimensional structure. The coordination polyhedra are described as a square antiprism. The solid complex emits green light under UV irradiation at room temperature with the quantum yield of 25%. Although Tb³⁺ is a non-Kramers ion, the alternating-current magnetic susceptibility showed frequency dependence in a 2000-Oe DC field, and the effective energy barrier for magnetization reorientation was 33(2) K. Thus, $[{Tb_2(C_4O_4)_3(H_2O)_8}_n]$ displayed functions of a potential luminescent magnet.

Keywords: rare earth metal; single-molecule magnet; single-ion magnet; luminescence; photoluminescence; crystal structure

1. Introduction

Squarate, a dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione ($C_4O_4^{2-}$, abbreviated as sq hereafter; Scheme 1), has two strongly polarized carbonyl groups to gain the stabilization energy of 2π aromaticity [1]. The negative charges are delocalized among four oxygen atoms which can serve as good O donors in coordination chemistry [2–4]. Metal sq salts are known to afford polymeric polynuclear complexes due to μ_2 - to μ_4 -modes of sq ligands. Owing to this bridging ability, sq has recently been used as a building block in metal–organic frameworks with various functionalities [5–9].



Scheme 1. Canonical structures of squarate (sq).

Transition metal sq salts are often subjected to studies on exchange-coupled magnetic materials, as exemplified with Ni²⁺ and Cu²⁺ salts [10]. Lanthanide (Ln) sq complexes have also been well-known and studied since the 1970s [11,12], thanks to the Ln-O affinity. Even neutral carbonyl compounds can ligate Ln ions [13]. In contrast to transition metal sq salts, Ln sq salts give a scarce chance to investigate 4f-4f superexchange interactions, because magnetic 4f orbitals are shielded with 5s, 5p, and 6s orbitals. The Weiss temperature of Gd³⁺ squarate was reported to be as small as –0.12 K [14]. Instead, single-ion magnets (SIMs) emerge as a next-generation material, especially when exchange coupling is negligible [15]. SIM behavior is regulated with a relatively slow magnetization reorientation, as a result of a large magnetic moment and strong magnetic anisotropy, which is found in heavy Ln ions, typically $_{65}Tb^{3+}$, $_{66}Dy^{3+}$, $_{67}Ho^{3+}$, and $_{68}Er^{3+}$ [16].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Meanwhile, Ln ions are available for various luminescent materials [17,18], owing to sharp and strong emission, and their coordination compounds have been applied to light-emitting diodes in lighting devices [19,20] and luminescent probes in biology [21]. The green-light emission from Tb^{3+} ion is popular, and the red to NIR luminescence from Eu^{3+} , Nd^{3+} , Sm^{3+} , Ho^{3+} , Er^{3+} , Yb^{3+} , etc. is of interest as well [22,23]. We aimed at materials showing multifunctionalities by using a Tb^{3+} ion. In this Communication, the crystal structure of terbium(III) squarate hydrate [$\{Ln_2(sq)_3(H_2O)_8\}_n$] (Ln = Tb; abbreviated as **Tb-sq** hereafter) has been determined for the first time. The photoluminescent and magnetic properties will be reported.

2. Materials and Methods

2.1. Preparation

Method A. An aqueous solution (10 mL) containing TbCl₃·6H₂O (Aldrich, 150 mg; 0.40 mmol) and an aqueous solution (10 mL) containing squaric acid (H₂sq) (Junsei Chemical, 69 mg; 0.60 mmol) were combined at room temperature and allowed to stand for a week. Very thin plates of **Tb-sq** were precipitated, and they were collected on a filter, washed with water, and air-dried. The yield was 94.3 mg (59%). Mp. > 300 °C. Anal (PerkinElmer 2400 II). Calcd.: C, 18.06; H, 2.02% for C₁₂H₁₆O₂₀Tb₂. Found: C, 18.11; H, 1.81%. IR (neat, attenuated total reflection (Nicolet FT-IR 6700)) 640, 664, 1093, 1463, 1602, 3089, 3404 cm⁻¹.

Method B. A hydrothermal synthesis technique was applied with a Parr Teflon autoclave in an As-one ON-300S thermostat dryer. A brown suspension containing $\text{Tb}^{\text{III}}_2\text{O}_3$ (Angene Chemical, 37 mg; 0.10 mmol), H₂sq (46 mg; 0.40 mmol), and water (10 mL) was heated at 150 °C for 72 h and then slowly cooled down to room temperature for 48 h. Off-white prismatic and powdery products were collected on a filter, washed freely with water, and air-dried. The yield was 69.0 mg (85%). The product was identical to **Tb-sq**, as confirmed by means of a powder X-ray diffraction (PXRD) study.

2.2. Structural Analysis

X-ray diffraction data of **Tb-sq** were collected on a Rigaku Saturn70 hybrid pixel array detector with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were directly solved by a heavy-atom method and expanded using Fourier techniques in the Olex2 1.3 program [24]. The parameters were refined on Shelxl [25]. Hydrogen atoms were located at calculated positions and treated as "riding". Selected data are as follows: C₁₂H₁₆O₂₀Tb₂, monoclinic *Pc*, *a* = 11.9331(8), *b* = 8.1820(6), *c* = 10.0563(7) Å, β = 96.103(6)°, *V* = 976.29(11) Å³, *Z* = 2, *d* = 2.715 g cm⁻³, μ (Mo K α) = 7.292 mm⁻¹, *R*(*F*) (*I* > 2 σ (*I*)) = 0.0247, *wR*(*F*²) (all reflections) = 0.0603, goodness-of-fit parameter = 1.020, *T* = 296(1) K for 4200 reflections. CCDC (Supplementary Materials) reference number 2108278.

The PXRD patterns were recorded on a Rigaku Ultima III diffractometer using Cu K α radiation ($\lambda = 1.54178$ Å) at room temperature.

2.3. Photoluminescent Measurements

The emission spectrum and the absolute quantum yield of polycrystalline **Tb-sq** were measured on a Hamamatsu Photonics Quantaurus-QY C11347 absolute PL quantum yield measurement system. The holder blank data were measured separately and subtracted from the raw sample data. The emission spectrum was recorded after the excitation wavelength was set to the excitation maximum.

2.4. Magnetic Measurements

Direct-current (DC) magnetic susceptibilities of **Tb-sq** were measured on a Quantum Design MPMS-XL7 SQUID magnetometer with a static field of 500 Oe. The magnetic responses were corrected with diamagnetic blank data of the sample holder measured separately. The diamagnetic contribution of the sample itself was estimated from Pascal's constants [26]. The alternating-current (AC) magnetic susceptibilities on **Tb-sq** were

recorded on a Quantum Design PPMS apparatus equipped with an AC/DC magnetic susceptibility option.

3. Results and Discussion

In the previous work [11,12,27,28], several pseudo-polymorphs are separated depending on the bridging mode of sq and the number of solvent (water) molecules ligating to metal ions and incorporated as a guest: $[{Ln_2(sq)_3(H_2O)_4}_n], [{Ln_2(sq)_3(H_2O)_{11}}_n] \cdot (H_2O)_2,$ $[Ln(Hsq)(sq)(H_2O)_6], [Ln(Hsq)(sq)(H_2O)_6] \cdot (H_2O), [{Ln_2(sq)_2(ox)(H_2O)_4}_n] (ox = oxalate),$ and **Ln-sq**. In the present study, such diversity was actually observed in the reactions from Tb and other Ln ions. However, we found that a dilute aqueous solution with a stoichiometric molar ratio according to Reaction Equation (1), namely TbCl₃ (0.2 mmol) and H_2 sq (0.3 mmol) in water (10 mL), is preferable to afford **Tb-sq** (Method A). As Figure 1a shows, the purity as a bulk solid was confirmed by means of PXRD.

$$2 \operatorname{TbCl}_3 \cdot 6H_2O + 3 \operatorname{H}_2\operatorname{sq} \longrightarrow \operatorname{Tb}_2(\operatorname{sq})_3(\operatorname{H}_2O)_8 + 6 \operatorname{HCl} + 4 \operatorname{H}_2O \tag{1}$$

Exp. Method A





Since Ln oxides are basic solids, organic acids such as H_2 sq ($pK_a = 2.2$) can dissolve them [29]. To avoid the formation of undesired compounds, protonated Hsq⁻ and partially decomposed ox²⁻, possibly caused by an acidic by-product, we utilized Tb₂O₃ as a starting material in hydrothermal synthesis (Method B), as described with Reaction Equation (2). A slightly excess amount of H_2 sq led to complete consumption of Tb₂O₃, and thus the following molar ratio is recommended; Tb₂O₃ (0.1 mmol) and H₂sq (0.4 mmol) in water (10 mL). The PXRD patterns (Figure 1a) clarify that both products from Methods A and B are identical. Polycrystalline **Tb-sq** obtained from Method B was satisfactorily pure, but a sample from Method A after being checked with elemental analysis was subjected to detailed physical measurements.

$$Tb_2O_3 + 3 H_2sq + 5 H_2O \longrightarrow Tb_2(sq)_3(H_2O)_8$$
(2)

The crystallographic analysis of **Tb-sq** was successful in a monoclinic *Pc* space group. Surprisingly, this is the first structural report on **Tb-sq**, despite the simple composition. However, we have to cite and compare practically the same structure with very close cell parameters for the Eu, Gd, Dy, and Er analogues. The report by Petit et al. [11] can be regarded as a pioneering work, and the space group of **Eu-sq** was determined to be *Pc*, while the possibility of centrosymmetric P2/c was rejected. Since then, the space groups reported were controversial; $P2_1/c$ was chosen for **Gd-sq** [14] with one sq missing, presumably owing to disordered weak electron density. For **Dy-** and **Er-sq** [28], $P2_1/c$ was assumed, but a severe overlap of the atomic coordinates remained. We encountered a similar centrosymmetry/non-centrosymmetry problem, and finally concluded that the most plausible space group is *Pc* based on the rational crystal structure (Figure 1b,c).

The asymmetric unit contains two Tb ions, three sq ions, and eight water ligands. The Tb-O distances vary from 2.331(8) to 2.449(7) Å. The polyhedra around the Tb ions are best described as an approximate square antiprism from the SHAPE analysis [30]; the CShM values for the Tb1 and Tb2 ions were 0.367 and 0.292, respectively, with reference to SAPR-8. Figure 1c illustrates that the local molecular axis of each Tb³⁺ polyhedron is aligned almost parallel in a crystal.

The crystal of **Tb-sq** consists of a bilayer structure parallel to the crystallographic *bc* plane (Figure 1c). Every sq bridges Tb ions. Squarate C1-C2-C3-C4 (abbreviated as sq1) binds three Tb1 ions with the O1, O3, and O4 coordination bonds, while three sq1 ions are coordinated to a Tb1 ion to form a Tb1/sq1-sheet parallel to the *bc* plane. Quite similarly, three Tb2 ions and three μ_3 -sq3 anions (C9-C10-C11-C12 squarate) construct a Tb2/sq3-sheet with the O9, O10, and O11 coordination bonds. Between the two sheets, another sq (sq2) interconnects Tb1 and Tb2 ions with the O5 and O8 donor atoms. Consequently, a sandwiched two-dimensional polynuclear polymer appears. The shortest intra-sheet Tb1•••Tb1 and Tb2•••Tb2 distances are 6.4246(5) and 6.4671(5) Å, respectively, which are comparable to the shortest inter-sheet Tb1•••Tb1 and Tb2•••Tb2 distances across O-C-C-O atoms. The shortest Tb1•••Tb1 and Tb2•••Tb2 distances across O-C-C-C-O atoms are somewhat longer (8.1820(6) Å, corresponding to the *b*-axis translation).

The sq rings are stacked along the *a* axis (Figure 2a). The presence of π - π interaction has already been discussed in **Eu-sq** [11]. In addition to this, dipolar interaction between the polarized carbonyl groups (Scheme 1) should be pointed out, because the shortest interplane distances are found between the C and O atoms in a slipped π - π overlap. Furthermore, the dense hydrogen-bonding network also contributes to stabilizing the crystal. Relatively short $O_{(w)} \bullet \bullet O_{(sq)}$ distances are depicted in Figure 2b-d. Seven-membered rings comprising O-C-C-O_(sq)-Tb-O-H_(w) atoms are an important motif. The oxygen atoms of H-donating water molecules are located nearly on the H-accepting sq molecular plane, indicating the sp²-hybridization of the sq oxygen atoms and the substantial O•••H interaction.



Figure 2. (a) Stacking motif of sq planes. The shortest interplane distances are indicated with dotted lines. (b) Hydrogen bonds around sq1, (c) sq2, and (d) sq3. The interatomic O•••O distances are indicated. The symmetry operation codes: E: x, 1+y, z; F: -1+x, 1-y, 1/2+z; G: 1+x, 1-y, -1/2+z.

Figure 3a shows the intense photoluminescence of a solid sample of **Tb-sq** under ambient conditions with irradiation from a handheld UV light (375 nm). The emission spectrum of **Tb-sq** at room temperature was recorded under irradiation at $\lambda_{ex} = 320$ nm (Figure 3b). Major luminescence peaks appeared at 490, 544, 583-588, and 620-621 nm, which are assigned to the f–f transitions of ${}^{5}D_{4} - {}^{7}F_{J}$ with J = 6, 5, 4, and 3, respectively [31]. The excitation spectrum of **Tb-sq** is superimposed in Figure 3b. A broad band at 300–360 nm corresponds to the absorption of the organic ligand. The solution absorption spectrum of Tb^{3+} squarate was reported to show a peak at 270 nm and a shoulder around 300 nm [32]. The polymeric solid form of **Tb-sq** seems to lead to a red shift in absorption. The quantum yield of the photoluminescence (Φ) was recorded with the emission monitored at 450–700 nm at room temperature (Figure 3c). Almost constant $\Phi = 0.25 - 0.24$ was found in the range $\lambda_{ex} = 310 - 350$ nm. The efficient photoluminescence can be accounted for with an antenna effect [33,34], which involves a sensitizing organic chromophore allowing indirect excitation of the Ln ion. The absorption from Ln ions themselves is usually weak, so that the organic UV-vis absorbents are necessary adjacent to the Ln ion. The luminescent bands were accompanied by fine structures, and further investigation would clarify the sublevel regulated with J^{z} [35–38].



Figure 3. (a) A photo of a solid sample of **Tb-sq** under irradiation of UV light (375 nm). (b) Emission spectrum ($\lambda_{ex} = 320$ nm) and excitation spectrum ($\lambda_{em} = 450-700$ nm) of polycrystalline **Tb-sq** recorded at room temperature. (c) Absolute photoluminescence quantum yield as a function of excitation wavelength.

Figure 4a displays the DC magnetic susceptibility result on a formula {Tb₂(C₄O₄)₃(H₂O)₈} basis of **Tb-sq**. At 300 K, the $\chi_m T$ value was 22.9 cm³ K mol⁻¹, in good agreement with the theoretical value 23.6 cm³ K mol⁻¹ expected for magnetically isolated Tb³⁺ ion from the total angular moment J = 6 and the Landé g factor $g_J = 3/2$. On cooling, the $\chi_m T$ value gradually decreased and reached 16.4 cm³ K mol⁻¹ at 1.8 K, and this finding can be explained in terms of the depopulation effect with respect to the J^z sublevels. The *M*-*H* curves (Figure 4a, inset) display a nearly saturated curve, but the apparent saturation magnetization (11.6 $N_A \mu_B$ at 7 T and 1.8 K when the sample was unfixed) was lower than the maximal value, 18 $N_A \mu_B$ from $J^z = 6$, mainly because of the strong magnetic anisotropy of Tb³⁺.

Figure 4b shows the in-phase and out-of-phase portions of the AC magnetic susceptibilities (χ'_{m} and χ''_{m} , respectively) for **Tb-sq**, measured at an applied DC field of 2000 Oe. No appreciable χ''_{m} was recorded without any applied field. Possible quantum tunneling of the magnetization is suppressed with a field bias [39]. The Arrhenius plot on **Tb-sq** is drawn in Figure 4c, using the frequency dependence of the χ''_{m} peak data. The effective activation energy (U_{eff}) for the magnetization reversal and pre-exponential factor (τ_0) were determined according to the equation, $\ln(1/2\pi\nu) = \ln(\tau_0) + U_{eff}/k_BT$ [40], giving $U_{eff}/k_B = 33(2)$ K and $\tau_0 = 8.1(40) \times 10^{-8}$ s. A straight line suggests that the magnetization would undergo Orbach-type relaxation [41]. In a lowest temperature region around 2 K, the χ''_{m} peaking temperature seems to become insensitive to frequency. The Cole–Cole plot [42] did not trace a simple semicircle; in fact, a second relaxation process may be operative. The origin of the additional behavior is unclear at present, and further investigation on Tb³⁺-sq-Tb³⁺ superexchange magnetic coupling, together with the energy potential surface regarding J^z , is now underway.

We have already reported another system, the Tb³⁺ complexes carrying "*mer*"- [tris(*N*-[(imidazol-4-yl)-methylidene]-*dl*-phenylalaninato) and related "*fac*"-*dl*-alaninato ligands [43]. These complexes exhibited luminescence and SIM behavior, but no blocking was recorded above 2 K in the same AC-field frequency window as that of the present study. Interestingly and ironically, a much simpler **Tb-sq** presents better SIM characteristics. This may be because the D_{4d} square-antiprism crystal field in **Tb-sq** is just suitable for SIM behavior, similarly to the Tb³⁺ phthalocyanino complex [15]. The oblate electron density around Tb³⁺ minimizes the energies at the large- $|J^z|$ sublevels to give a double-well potential, although Tb³⁺ is a non-Kramers ion, when the square-antiprism crystal field is axially compressed [44].



Figure 4. (a) Temperature dependence of $\chi_m T$ for **Tb-sq**, measured at 500 Oe. The sample was fixed with a small amount of eicosane for removing the field-align effect due to torqueing. Inset: *M*–*H* curves for **Tb-sq**, measured at 1.8 K with and without eicosane. (b) AC magnetic susceptibilities for **Tb-sq** at an applied DC field of 2000 Oe. Solid lines are drawn as a guide for the eye. (c) Arrhenius plot for **Tb-sq** with the data taken from (b). For a solid line, see the text. (d) Cole–Cole plots for **Tb-sq**. Solid lines are drawn as a guide for the eye.

4. Conclusions

We prepared **Tb-sq** in two ways and found that a hydrothermal synthesis from Tb₂O₃ would be an excellent method for specific synthesis. The crystal structure of **Tb-sq** was determined in a monoclinic *Pc* space group. A sandwiched two-dimensional structure was characterized. The solid complex emits green light under UV irradiation at room temperature with the quantum yield of 25%. The AC magnetic susceptibility measurement showed frequency dependence, as an indication for a SIM with U_{eff}/k_B = 33(2) K in a 2000-Oe DC field. It seems to be related with a D_{4d} crystal field from the square-antiprism coordination structure around Tb³⁺. Compound **Tb-sq** is an easily obtainable and prototypical luminescent magnet. More sophisticated compounds [45] will be designed and synthesized from the viewpoint of J^z energy surface engineering to explore magnet-based multi-functional Ln coordination materials.

Supplementary Materials: CCDC deposition number 2108278 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/structures.

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